

# Complex electrochemical processing of technogenic wastes of rhenium-containing heat-resistant nickel alloys\*

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The complex electrochemical processing in sulfuric acid solutions of technogenic wastes of rhenium-containing heat-resistant nickel alloys (HRNA) in the form of rather large scrap pieces of turbine blades has been studied. It was found that anodic dissolution of large waste pieces of rhenium-containing HRNA can be successfully carried out in sulfuric acid solutions (100 g/dm<sup>3</sup>) with addition of nitric acid (20 g/dm<sup>3</sup>) under direct current with a current density of 500–1000 A/m<sup>2</sup> and a temperature of 30–40 °C without preliminary preparation. As much as 80–90% of rhenium, 90–95% of nickel, cobalt, chromium and aluminum pass into solution under these conditions. Almost all refractory rare metals (tungsten, tantalum, hafnium) pass into the anode slime almost completely.

Rhenium, nickel and cobalt remaining in the anode slime were converted into solution by chemical slime treatment in a 2 M sulfuric acid solution with the nitric acid additives. Rhenium in the form of crude ammonium perrhenate, where rhenium content is not less than 68.9 wt.%, has been recovered from the combined solution after anodic treatment of alloy wastes and chemical dissolution of anode slimes by a known solvent extraction method. The cake, remaining after chemical treatment of anode slimes, is a concentrate of refractory rare metals containing, wt.%: up to 39–42 W; 15–18 Ta; 3–4 Hf. According to X-ray fluorescence (XRF) analysis, the cake base is tungsten trioxide. Following rhenium extraction, the sulphate raffinate, containing significant amounts of nickel, cobalt, chromium, aluminum and some other metals, has been neutralized with alkali which allowed to precipitate hydroxides of these metals into a nickel-cobalt concentrate which includes 37.55% Ni and 4.48% Co. Roasting of nickel-cobalt concentrates obtained from the products of the HRNA waste electrochemical treatment at a temperatures of up to 400 °C will allow one to convert all non-ferrous metal hydroxides into oxides, reduce the mass of concentrates by 15–20%. The process flowsheet of complex processing of large-scale waste of rhenium-containing HRNA is proposed. The technology was successfully tested within the pilot project at the enterprise of RSE "Zhezkazganredmet", which is an internationally known manufacturer of ammonium perrhenate.

**Key words:** technogenic wastes, rhenium-containing heat-resistant nickel alloys, complex electrochemical processing, sulfuric solution, anode slime, rhenium, ammonium perrhenate, nickel-cobalt concentrate, concentrate of refractory rare metals.

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## Introduction

At present, the problem of the recycled raw resources conservation and their integrated use is becoming increasingly important in the overall balance of the world metal production. Waste from the processing and operation of heat-resistant nickel alloys (HRNA), which are used to make the blades of power turbines and jet engine turbines, is one of the most valuable types of secondary raw materials. Alloys are high-melting, high-strength and very resistant to material abrasion; they contain, wt.%: up to 50–75 Ni, 3–15 Co, as well as Cr, Al, and 1–10 wt.% of one or more elements from the Ta, Nb, W, Mo, Re, Pt, and Hf series [1–3].

The presence of up to 9% of rhenium in the alloys makes these wastes a promising type of the recycled rhenium raw material [2–24]. Along with expensive rhenium,

the extraction of other valuable non-ferrous and rare metals is also of interest. Recovery of valuable metals from the waste of these alloys presents a challenge. This is especially true for processing large waste pieces, such as scrap parts of gas turbine engines. If the waste in the scrap form is not contaminated, it can be remelted into the same alloy. General Electric Aviation (USA) has launched its own technology for rhenium recycling from the used high-pressure turbine blades, ensuring thereby the spent equipment picking from its customers around the world. Thanks to the closed cycle of waste processing, the company has reduced capital costs for manufacturing of new products and has reached leading positions in the processing of waste of rhenium-containing alloys. The production facilities for rhenium recycling from waste alloys also operate in Canada, Germany, Estonia, and the Czech Republic [4].

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Direct remelting doesn't suit for processing most of the waste, so process flowsheet including both pyro- and hydrometallurgical operations are used for their utilization with rhenium recovery [2–24]. The problem of crushing the wastes for their hydrometallurgical opening is solved using different techniques. For example, alloying the material with granulated aluminum in an induction furnace at 1500–1700 °C, or sintering the source material with an oxidizing furnace charge followed by leaching [4–6, 19]. A method of the valuable metals recuperation from superalloys is also proposed [12]; according to it, metal superalloys are decomposed in the melt of the alkali element salt. The superalloy melt decomposition product is crushed and leached in water. Valuable metals, such as tungsten, tantalum and rhenium, are extracted from the resulting solution and insoluble precipitate by various methods.

For the lump HRNA waste there are often suggested electrochemical methods based on the material anodic dissolution in solutions of inorganic acids under the action of DC or AC currents with conversion either rhenium or nickel-base of alloy into the solution with the rhenium concentration in the anode slime [2–24]. Rhenium can be separated from the rhenium-containing solutions obtained in one way or another by extraction and/or sorption methods [5–7, 13, 20]. The process of the ZhS-32VI (ЖС-32ВИ) alloy waste electrochemical leaching in a nitric acid electrolyte at the controlled cathode potential was studied [16], which allowed to obtain metallic nickel concentrate of a 95–97% purity or nickel-rhenium precipitate with the rhenium content of 8–12%. There has been proposed a method for electrochemical processing of a rhenium-containing heat-resistant alloy, which includes its dissolution at the controlled anode potential and precipitation on the cathode from the resulting solution of nickel-cobalt concentrate [14–15].

Notwithstanding quite essential number of proposed schemes for recycling of rhenium and other valuable metals from the HRNA waste, the development of effective technologies for the multicomponent HRNA waste recycling remains the topical problem to date.

This paper presents the results of research on the complex electrochemical processing of technogenic waste of rhenium-containing heat-resistant nickel alloys, which are rather big scrap pieces of turbine blades.

### Experimental techniques

The subject of our inquiry was technogenic waste of heat-resistant nickel alloys in the form of large scrap pieces of turbine blades. Initially, large HRNA waste pieces were sawn off into smaller bits using an angle grinder for carrying out the analysis and experiments on treatment of these alloys. The experiments were performed in a temperature-controlled cell with platinum cathode; the sawn off HRNA bits, which were weighed before and after the dissolution operation, were used as anode. Anodic dissolution of the samples was fulfilled in sulfuric acid electrolytes of various compositions at a current density

of 1000 A/m<sup>2</sup>, a temperature of 30 °C, and duration of 3 hours. Magnetic stirrer mixed the solution in the cell.

Anodic dissolution of large scrap pieces (weighing up to 2 kg) was carried out in a specially designed 10 dm<sup>3</sup> electrolyzer with titanium cathode in a commercial-grade sulphuric acid solution with addition of nitric acid at an anode current density of 500–1000 A/m<sup>2</sup>. Mixing of the solution in the electrolyzer was carried out applying compressed air.

In the process of the HRNA waste anodic dissolution there were observed the formation of anode slime, which contains all the alloy-forming elements in its composition. The ratio of the dissolved alloy mass to the resulting slime mass is an important factor, since obtaining a large amount of slime will lead to additional expenditures for its further processing.

For additional rhenium, nickel and some other metals conversion into solution, chemical dissolution of anode slime was carried out in a commercial-grade sulphuric acid solution with addition of nitric acid. Rhenium was extracted from the combined sulfuric acid solutions obtained in the process of anodic dissolution of alloy waste and chemical dissolution of anode slimes by a well-known extraction method. Trialkylamine (TAA) with kerosene and 2-ethylhexanol was used as an extractant. Rhenium was re-extracted with an ammonia solution.

Nickel-cobalt concentrate was precipitated with alkalis from the sulphuric acid raffinates remaining after rhenium extraction recovery and containing significant amounts of nickel, cobalt, chromium, aluminum and some other metals.

Determination of the chemical and phase composition of the wastes of heat-resistant alloys and their products (solutions, anode slime, cake, crude ammonium perhenate, nickel-cobalt concentrate) was performed using X-ray fluorescence (the wavelength dispersive Panalytical Axios spectrometer), X-ray phase (the Bruker D8 Advance is a Cu/Mo-source, theta-theta diffractometer, Cu radiation, K $\alpha$ ), chemical (the PerkinElmer OPTIMA 2000™ DV atomic emission spectroscope), electron-microscopic (the JEOL JXA-8230 electron probe microanalyzer), IR-spectroscopic (the Thermo Nicolet Avatar 370 FTIR Spectrometer), thermal (the simultaneous thermal analyzer NETZSCH STA 449 F3; the results were processed by the NETZSCH Proteus® software) analysis methods.

### Results and discussion

The study of anodic dissolution in an electrochemical cell of small pieces (weighing up to 10 g) of alloy waste in sulfuric acid solutions with various additives was carried out. According to X-ray fluorescence analysis (XRF), the HRNA waste contains, wt. %: Re — 2.28; Ni — 56.14; W — 8.01; Mo — 0.42; Co — 7.89; Al — 6.04; Cr — 4.84; Ta — 2.85; Hf — 0.79; Si — 1.04. According to the XRF results, the base of alloys is solid solution of Re, W, Ta in nickel; it has a cubic lattice (parameter  $a = 0.3585$  nm, Ni = 0.3524 nm).

The research results showed that the highest rates of rhenium and nickel conversion into solution (up to 80–100%) were obtained with the use of a sulfuric acid solution with the nitric acid additives as an electrolyte (Fig. 1) at an anode current density of up to 1000 A/m<sup>2</sup> and a temperature of 25–30 °C. At the same time, there was also less formation of anode slime, which will reduce additional expenditures during its further processing.

Subsequent study of anodic treatment of larger HRNA waste pieces were conducted with the waste of alloys from another batch containing, according to XRF, wt.%: Re – 2.06; Ni – 56.04; W – 6.53; Mo – 0.51; Co – 7.55; Al – 6.04; Cr – 6.05; Ta – 2.70; Hf – 0.71; Si – 1.10.

Anodic dissolution of scrap pieces of turbine blades (weighing 140–220 g) was performed in a 10 dm<sup>3</sup> electrolyzer in a commercial-grade sulphuric acid solution (100 g/dm<sup>3</sup>) with addition of nitric acid (20 g/dm<sup>3</sup>) at an anode current density of 500–1000 A/m<sup>2</sup>. Mixing of the solution was carried out applying compressed air. The total alloy waste load was 667.58 g. Anodic dissolution of the waste was performed until the rhenium concentration in the solution was 0.1–0.3 g/dm<sup>3</sup>, then electrolysis was stopped, the resulting solution was completely poured out, and the electrolyzer was again filled up with the acid solution to dissolve the remaining waste. In total, 50 hours were spent on dissolving of the alloy waste in this experiment. The non-dissolved waste residue was 38.05 g. In total, 629.53 g of waste were dissolved, which was 94.3% of the initial waste weight. The mass of the resulting slime is 120.16 g. The dissolved alloy mass to the slime mass ratio was 5.23. According to XRF, the anode slime contains, wt.%: 1.99 Re; 4.45 Ni; 0.43 Co; 32.49 W; 14.13 Ta; 3.6 Hf; 1.58 Mo; 0.25 Al; 0.98 Cr.

The sulfuric acid solutions obtained from anodic dissolution of alloys were combined and filtered out. Blended solution is dark blue, transparent. The total volume of solutions was 14.38 dm<sup>3</sup> with the content, g/dm<sup>3</sup>: 0.73 Re; 24.18 Ni; 3.28 Co; 2.62 Al; 1.54 Cr; 0.15 W; 0.07 Mo. The power consumption for dissolving of 1 kg of alloy waste was 9.6 kW·h. The recovery of rhenium and some other elements into solution and slime during the HRNA waste anodic dissolution in a commercial-grade sulphuric acid solution with addition of nitric acid is shown in Table 1. Nickel, cobalt, aluminum and chromium, as well as over 80% of rhenium, pass into solution almost completely. Tungsten, tantalum, hafnium and most part of molybdenum completely pass to the anode slime.

The initial raw material comprised 6 types of HRNA alloy samples of different weights, which also varied in the content of main elements in them, wt.%: 44.81–62.07 Ni; 6.57–8.75 Co; 1.95–2.72 Re; 0.57–1.68 Mo; 5.05–13.08 W; 2.96–12.43 Ta; 0.67–0.78 Hf; 4.46–7.14 Cr; 0.16–0.64 Si.

Experiments were performed at current densities of 1000 and 500 A/m<sup>2</sup> for 10 hours. Stirring of the solution was carried out applying compressed air. To more accurately determine the effect of current density on the anodic

dissolution process in the experiments, equal amount of each type of waste samples was loaded into the electrolyzer. The results are represented in Table 2.

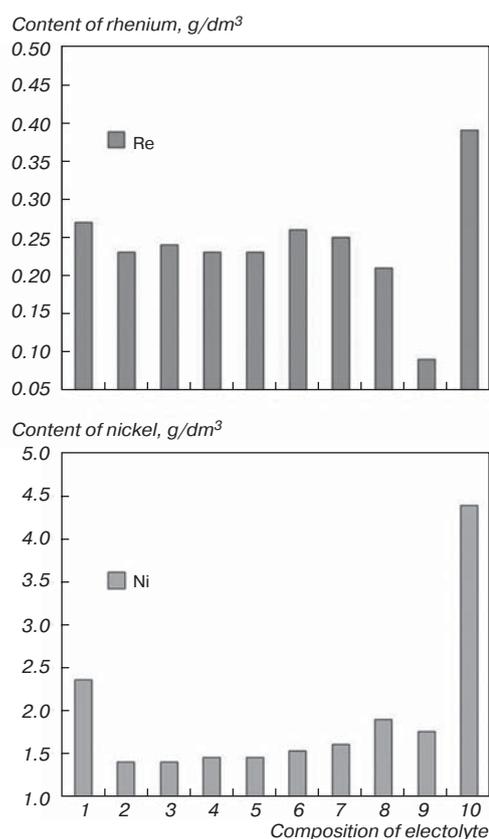


Fig. 1. Dependence of the rhenium and nickel content in solutions after anodic dissolution of the waste of heat-resistant nickel alloys upon the initial content of electrolytes, g/dm<sup>3</sup>: 1 – 100 H<sub>2</sub>SO<sub>4</sub>; 2 – 10 H<sub>2</sub>SO<sub>4</sub>; 70 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; 125.2 Na<sub>2</sub>SO<sub>4</sub> × 10H<sub>2</sub>O; 3 – 20 H<sub>2</sub>SO<sub>4</sub>; 40 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; 90.7 Na<sub>2</sub>SO<sub>4</sub> · 10H<sub>2</sub>O; 4 – 20 H<sub>2</sub>SO<sub>4</sub>; 40 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; 90.7 Na<sub>2</sub>SO<sub>4</sub> · 10H<sub>2</sub>O; 20 NaCl; 5 – 20 H<sub>2</sub>SO<sub>4</sub>; 40 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; 90.7 Na<sub>2</sub>SO<sub>4</sub> · 10H<sub>2</sub>O; 20 HCl; 6 – 150 H<sub>2</sub>SO<sub>4</sub>; 7 – 200 H<sub>2</sub>SO<sub>4</sub>; 8 – 150 H<sub>2</sub>SO<sub>4</sub>; 20 NaCl; 9 – 200 H<sub>2</sub>SO<sub>4</sub>; 30 NaCl; 10 – 150 H<sub>2</sub>SO<sub>4</sub>; 3(HNO<sub>3</sub>)

Table 1  
The degree of recovery of some elements into the electrolysis products on the HRNA waste anodic treatment in a commercial-grade sulphuric acid solution (100 g/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>) with addition of nitric acid (20 g/dm<sup>3</sup>)

Element	Recovery, %			
	into solution	into slime	Total	Imbalance
Re	81.2	18.5	99.7	-0.3
Ni	98.4	1.5	99.9	-0.1
Co	99.2	1.1	100.3	+0.3
W	4.9	100.9	105.8	+5.8
Mo	31.6	70.9	102.5	+2.5
Al	99.0	0.8	99.8	-0.2
Cr	92.2	6.9	99.1	-0.9
Ta	0.1	100.2	100.3	+0.3
Hf	-	100.2	100.2	+0.2

Table 2

**The current density influence on the results of a 10 h anodic dissolution of HRNA waste**

Anodic current density, A/m <sup>2</sup>	Weight of the fed waste, g	Re content in the solution, g/dm <sup>3</sup>	The dissolved waste in all, g	Weight of the dry anode slime, g	The dissolved alloy mass to anode slime mass ratio	Power consumption, kW·h		The waste dissolution rate, g/h
						total	per 1 kg of HRNA	
1000	2490	1.80	625	176	3.55:1	4.440	7.10	62.5
500	2510	1.42	521	137	3.80:1	2.368	4.55	52.1

It follows from the data of Table 2 that the HRNA waste dissolution rate at a current density of 1000 A/m<sup>2</sup> is higher than that at 500 A/m<sup>2</sup>, but power consumption per 1 kg of waste is higher as well. Up to 80–85% of rhenium, about 90–95% of nickel, cobalt, chromium and aluminum pass into solution. Tungsten, tantalum, and hafnium pass to the anode slime almost completely. According to XRF, the slimes obtained in the HRNA waste anodic dissolution process at current densities of 1000 and 500 A/m<sup>2</sup> contain, respectively, wt. %: 1.27 Re; 25.36 Ni; 1.83 Co; 0.9 Mo; 21.37 W; 12.30 Ta; 1.80 Hf and 1.05 Re; 26.67 Ni; 2.03 Co; 0.7 Mo; 21.85 W; 12.31 Ta; 1.83 Hf.

In these experiments, the ratio of the dissolved alloy mass to the resulting anode slime mass at a current density of 500 A/m<sup>2</sup> is slightly higher than that at a current density of 1000 A/m<sup>2</sup>. This can be explained by the fact that the higher is current density on the surface of the dissolved sample, the more rapid are oxygen release and temperature increase. At that, destruction of a sample is faster due to the formation of numerous cracks. The ratio of the dissolved alloy mass to the resulting anode slime mass also depends on the structure, chemical and phase composition of alloys.

To recover rhenium, nickel and cobalt from anode slime, the latter was chemically dissolved in a 2 M solution of a commercial-grade sulphuric acid solution with addition of nitric acid (50 g/dm<sup>3</sup>). The received results showed that the most part of rhenium, nickel, cobalt and aluminum is mainly transferred to the solution on chemical treatment of the slime. Average content of elements in the filtrates is as follows, g/dm<sup>3</sup>: 0.27 Re; 4.53 Ni; 0.39 Co; 0.31 Al; 0.06 W; 0.07 Mo; 0.20 Cr. The undissolved cake of light gray color was filtered and washed with water. The cake weight was about 62% of the initial mass of the slime to be dissolved. According to the XRF data, the cake has contained, wt. %: 42.45 W; 17.64 Ta; 3.62 Hf; 1.21 Re; 1.3 Mo; 1.0 Cr; 0.99 Ni; 0.11 Co; 0.17 Al; 0.04 Si; 36.66 O. According to XRF, the base of the cake is tungsten trioxide.

Solutions from anode treatment of waste and chemical dissolution of slime were combined. The element content in the blend was, g/dm<sup>3</sup>: 0.86 Re, 23.11 Ni, 3.17 Co, 2.31 Al, 0.08 W, 0.08 Mo, 2.31 Cr. A part of the combined sulphuric acid solution was taken for rhenium recovery. Trialkylamine (TAA) with kerosene and 2-ethylhexanol was used as an extractant (its composition is, vol. %: TAA – 10.0, alcohol – 10.0, kerosene – 80.0). The rhenium recovery conditions was as follows: O:W = 1:8; contact time – 5 min; the room temperature. The separation of phases occurred quickly enough. Rhenium recovery into the organic phase was 98.3%. Rhenium re-extraction was performed with a 2.5 M ammonia solution at O:W = 4:1, contact time – 5 min; the room temperature. The separation of phases occurred quite quickly. Rhenium recovery into an ammonia solution was above 99.4%. The ammonia re-extract was evaporated, then a fine-grained deposit of white color with gloss fell out on cooling the solution. The deposit was analyzed by X-ray phase, X-ray fluorescence and spectral methods. The results has showed that the received salt is crude ammonium perrhenate of a very good quality, with a rhenium content of at least 68.9 wt.%, and the impurities, wt. %: 0.001 Ni; 0.001 Co; 0.001 Al; 0.005 W; 0.002 Mo; 0.001 Cr.

After rhenium extraction recovery from the solutions of the alloy waste anodic treatment and chemical treatment of slimes, there remain sulphate raffinate, containing significant amounts of nickel, cobalt, chromium, aluminum and some other metals. To recover these metals from refined products, the method of precipitation of metal hydroxides with alkalis was used [23–24].

NaOH solution (500 g/dm<sup>3</sup>) as a precipitator was added in the solution of raffinate containing, g/dm<sup>3</sup>: 14.26 Ni; 2.48 Co; 0.02 Re; 0.12 Mo; 0.02 W; 1.81 Al; 2.21 Cr (acidity of 95.06 g/dm<sup>3</sup>) under continuous stirring and at a temperature of 40 °C until pH 8–9 was established.

Then the mixing process was continued for 1 hour. The resulting precipitate was filtered, washed with water, dried at a temperature of 105 °C to achieving a constant weight, and then physical and chemical researches on the precipitate were performed [24]. According to the XRF data, the resulting precipitate, which can be considered a nickel-cobalt concentrate, contains, wt. %: 37.55 Ni; 4.48 Co; 2.41 Al; 4.24 Cr, 0.02 W; 0.22 Mo; 3.65 S; 2.11 Na; 0.21 Si; 43.33 O. According to the XRF data, the following phases are present in dry Ni – Co concentrate: 33 wt. % of Na<sub>2</sub>SO<sub>4</sub>; the rest is Ni<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O; Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub>; NiSO<sub>4</sub>(H<sub>2</sub>O)<sub>7</sub>; NiSO<sub>4</sub>·6H<sub>2</sub>O; CoSO<sub>3</sub>·3H<sub>2</sub>O. Thermogravimetric analysis of concentrates has showed that the processes of dehydration of nickel, cobalt, chromium, aluminum hydroxides and their transition to oxide forms take place in the temperature range of 300–400 °C. Roasting of nickel-cobalt concentrates obtained from the products of electrochemical treatment of the HRNA waste at a temperature of up to 400 °C will allow

to convert all non-ferrous metal hydroxides into oxides, to reduce the mass of concentrates by 15–20%. The burnt nickel-cobalt concentrates can be used in the smelting of some ferroalloys.

Fig. 2 shows the process flowsheet of complex processing of large pieces of the rhenium-containing HRNA waste without preliminary preparation. It includes anodic dissolution of waste under the action of direct current in sulfuric acid solutions and obtaining of crude ammonium perrhenate, concentrate of refractory rare metals and nickel-cobalt concentrate from the products of electrolysis.

To test the technology in working environment of RSE “Zhezkazganredmet”, which has been ranked third in the world for the production of ammonium perrhenate until 2010, a 100 dm<sup>3</sup> pilot-industrial electrolyzer was manufactured. The tests have been carried out in the rare metals shop in accordance with the process flowsheet for the HRNA waste processing shown in Fig. 2.

The testing involved performing of the following operations: anodic dissolution of the HRNA waste pieces in a commercial-grade sulphuric acid solution (100 g/dm<sup>3</sup>) with addition of nitric acid (20 g/dm<sup>3</sup>) under the action of DC with producing of rhenium-containing solution and anode slime; chemical dissolution of the anode slime in a 2 M solution of commercial-grade sulphuric acid with addition of nitric acid to get insoluble cake, representing a concentrate of rare refractory metals; extraction recovery of rhenium from the combined solutions of the HRNA waste anode opening and the anode slime chemical dissolution; precipitation of nickel-cobalt concentrate from the sulphate raffinate after rhenium extraction by sodium hydroxide solution.

The HRNA waste anodic dissolution was performed at a current density of up to 1000 A/m<sup>2</sup>, since this creates

a smaller amount of anode slime, which further reduces the expenditures for its processing, and rather high current yield is achieved. Samples of the solution for the content of rhenium and acid have been taken every hour. After 4 hours of electrolysis, the rhenium content in the solution has averaged 0.4–0.7 g/dm<sup>3</sup>. The solution was poured out from the electrolyzer into a storage container. Periodically, the HRNA pieces have been reloaded into the electrolyzer, fresh acid solution has been filled up and then the dissolution process was continued.

During 282 hours of operation with the stops for discharge of the produced solutions and reloading of waste in a 100 dm<sup>3</sup> pilot electrolyzer, a volume of the processed HRNA waste was 134.68 kg in total. The undissolved waste residue mass was 4.26 kg. Dissolved was 130.42 kg of waste in all. The weight of anode slime amounted to 23.32 kg, and the dissolved waste mass to anode slime mass ratio was 5.59:1. The rate of the HRNA waste anodic dissolution has ranged from 0.355 to 0.683 kg/h. Power consumption for dissolving of 1 kg of the HRNA waste has ranged from 7.9 to 11.75 kW·h.

The obtained anode slimes were chemically dissolved in a 2 M commercial-grade sulphuric acid solution with addition of nitric acid. Up to 70% Re and 90% Ni and Co have passed from anode slimes into the resulting filtrate, as well as 16.82 kg of a concentrate of refractory rare metals (tungsten-tantalum concentrate) with a content of 35.97% W and 21.29% Ta.

The solutions after the HRNA waste anodic treatment and chemical dissolution of anode slimes were combined with the water after washing the concentrate of refractory rare metals and directed to the solvent extraction of rhenium according to the existing technology in the shop of rare metals. The resulting rhenium-containing organic

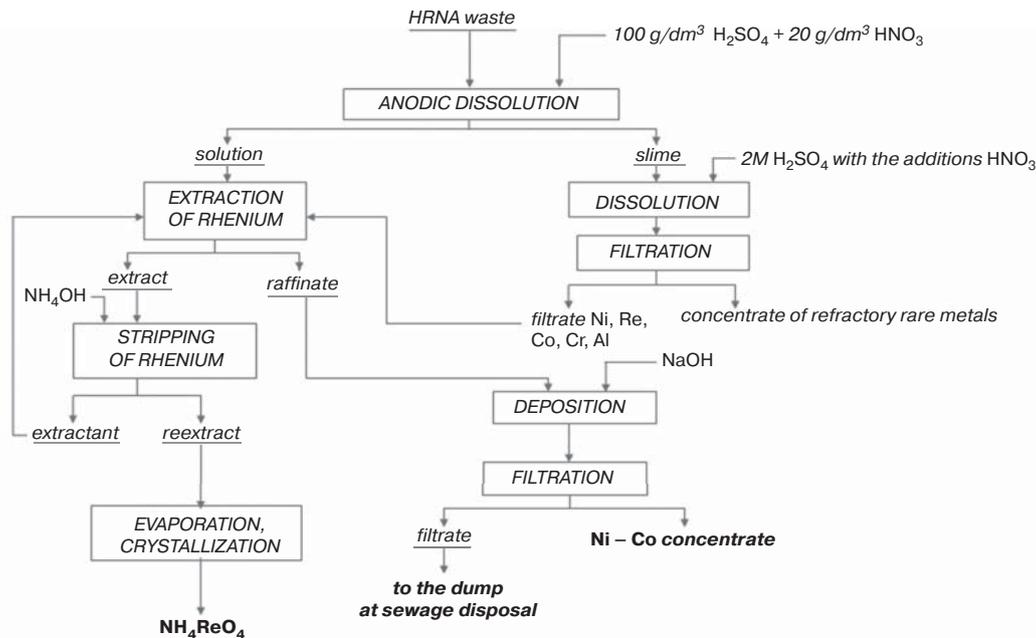


Fig. 2. The process flowsheet of complex processing of the wastes of rhenium-containing heat-resistant nickel alloys

matter was directed to a solid phase stripping, in the process of which a pulp of crude ammonium perrhenate was formed, and crude ammonium perrhenate with a content of 68.4% Re was obtained from it.

Nickel-cobalt concentrate was precipitated from the raffinate after extraction of rhenium with a solution of sodium hydroxide, which was filtered and washed with water to remove sodium sulfate and alkali residues. A total of 191.41 kg of nickel-cobalt concentrate with a content of 38.23% Ni and 5.16% Co was produced.

Based on the results obtained, the balance for rhenium, nickel, cobalt, tungsten and tantalum was compiled. Some of the consumption indices for the HRNA waste processing operations have been determined.

### Conclusions

The investigations have shown that anodic dissolution of large pieces of rhenium-containing HRNA waste without their preliminary preparation can be successfully carried out in sulfuric acid solutions with addition of nitric acid under direct current at a current density of 500–1000 A/m<sup>2</sup> and at a temperature of 30–40 °C. Up to 80–90% of rhenium and 90–95% of nickel, cobalt, chromium and aluminum pass into solution under these conditions. Almost all refractory rare metals (tungsten, tantalum, hafnium) pass to the anode slime.

Rhenium, nickel and cobalt, remaining in the anode slime, were converted to a solution by chemical treatment of the slime in a sulfuric acid solution with the nitric acid additives.

Rhenium in the form of crude ammonium perrhenate was recovered from the combined solutions after the HRNA waste anode treatment and chemical dissolution of anode slimes by a well-known solvent extraction method. The cake remaining after chemical treatment of anode slimes is a concentrate of refractory rare metals as a whole. After solvent extraction of rhenium, the sulphate raffinate, containing significant amounts of nickel, cobalt, chromium, aluminum and some other metals, has been neutralized with alkali, which allowed to completely precipitate the hydroxides of these metals into a nickel-cobalt concentrate. Roasting of nickel-cobalt concentrates obtained from the products of electrochemical processing of the HRNA waste at a temperature of up to 400 °C will allow to convert all non-ferrous metal hydroxides into oxides, reducing the mass of concentrates by 15–20%.

The process flowsheet of complex processing of the large-scale wastes of rhenium-containing heat-resistant nickel alloys is proposed. The technology was successfully tested in a pilot mode at the enterprise of RSE “Zhezkazganredmet”.

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